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(54) Title: PROCESS FOR MAKING ALKYL BENZENESULFONATE SURFACTANTS FROM ALCOHOLS AND PRODUCTS THEREOF (57) Abstract The present invention is in the field of processes for making modified alkylbenzenesulfonate surfactants and of the products of such processes, including the surfactant compositions and consumer cleaning products, especially laundry detergents, containing them. The processes herein have in common: (a) the provision of a specific, lightly branched alcohol mixture and (b) alkylation reaction of benzene, toluene or the like with this alcohol mixture using specific shape-selective zeolite catalysts, preferably at least partially dealuminized nonfluoridated H-mordenites. The alcohol required in the process can be prepared by any of (i) selective hydroformylation of lightly branched olefins; (ii) nonselective hydroformylation of linear olefins; and (iii) reactions of suitable alkyl Grignard reagents with methyl alkyl ketones.		

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PROCESS FOR MAKING ALKYL BENZENESULFONATE SURFACTANTS FROM ALCOHOLS AND PRODUCTS THEREOF

FIELD OF THE INVENTION

The present invention is in the field of processes for making modified alkylbenzenesulfonate surfactants or the corresponding alkyltoluene or alkyl naphthalene analogs and of the products of such processes, including the surfactant compositions and consumer cleaning products, especially laundry detergents, containing them. The processes herein have in common (a) the provision of a specific, lightly branched alcohol mixture and (b) alkylation reaction of benzene, toluene or the like with this alcohol mixture using specific shape-selective zeolite catalysts, preferably at least partially dealuminized nonfluoridated H-mordenites. The alcohol required in the process can be prepared by any of (i) selective hydroformylation of lightly branched olefins; (ii) nonselective hydroformylation of linear olefins; and (iii) reactions of suitable alkyl Grignard reagents with methyl alkyl ketones.

BACKGROUND OF THE INVENTION

Historically, highly branched alkylbenzenesulfonate surfactants, such as those based on tetrapropylene (known as "ABS" or "TPBS") were used in detergents. However, these were found to be very poorly biodegradable. A long period followed of improving manufacturing processes for alkylbenzenesulfonates, making them as linear as practically possible ("LAS"). The overwhelming part of a large art of linear alkylbenzenesulfonate surfactant manufacture is directed to this objective. Large-scale commercial alkylbenzenesulfonate processes in use in the U.S. today are directed to linear alkylbenzenesulfonates. However, linear alkylbenzenesulfonates are not without limitations; for example, they would be more desirable if improved for hard water and/or cold water cleaning properties.

In the petroleum industry, various processes have more recently been developed, for example for producing low viscosity lube oil, which the inventors have now discovered provide new insight on how to delinearize hydrocarbons to a limited and controlled extent. Such deliberate delinearization, however, is not a feature of any current

commercial processes in the different field of alkylbenzenesulfonate surfactant manufacture for consumer products. This is not surprising, in view of the overwhelming volume of LAS surfactant art teaching toward linear compounds and away from delinearization.

The majority of commercial processes for making alkylbenzenes rely on HF or aluminum chloride catalyzed alkylation of benzene. Quite recently, it has been discovered that certain zeolite catalysts can be used for alkylation of benzene with olefins. Such a process step has been described in the context of otherwise conventional processes for manufacture of linear alkylbenzenesulfonates. For example, the DETAL® process of UOP uses a zeolite alkylation catalyst. The DETAL® process and all other current commercial processes for alkylbenzenesulfonate manufacture are believed to fail to meet the internal isomer selectivity requirements of the inventive process and alkylation catalyst defined hereinafter. Moreover, the DETAL® process catalyst or catalysts are believed to lack the moderate acidity and intermediate pore size of alkylation catalysts used in the processes of the present invention. Other recent literature describes the use of mordenite as an alkylation catalyst, but no such disclosure makes the combination of specific process steps required by the instant invention. Moreover, in view of the linearity desired in alkylbenzenesulfonate products of conventionally known processes, they also generally include steps directed to the provision or making of a substantially linear hydrocarbon, not a delinearized one, prior to the alkylation. A possible exception is in US 5,026,933 which includes, for example, oligomerization of lower olefin such as propylene under narrowly defined conditions using collidine-deactivated ZSM-23 to form a composition comprising a tetramer assertedly having 1.3 methyl branches per chain, followed by fractionation and an alkylation using mordenite catalyst. See Example XVII. See also US 4,990,718 in which an alkylbenzene is made via a process that produces a vinylidene olefin by dimerization in presence of chromium catalyst but in which the vinylidene yield is adversely affected by oligomerization and in which distillation is required prior to alkylation. However, the processes of '933 and '718 have numerous shortcomings from the standpoint of the detergent industry in terms of cost, catalyst limitations in the propylene oligomerization or olefin dimerization stage,

presence of large volumes of distillation fractions that would need to be discarded or find nondetergent customers, and limited range of product compositions, including mixtures of chainlengths attainable. Such developments by the petroleum industry are, in short, not optimal from the standpoint of the expert formulator of detergent products.

BACKGROUND ART

US 5,026,933; US 4,990,718; US 4,301,316; US 4,301,317; US 4,855,527; US 4,870,038; US 2,477,382; EP 466,558, 1/15/92; EP 469,940, 2/5/92; FR 2,697,246, 4/29/94; SU 793,972, 1/7/81; US 2,564,072; US 3,196,174; US 3,238,249; US 3,355,484; US 3,442,964; US 3,492,364; US 4,959,491; WO 88/07030, 9/25/90; US 4,962,256, US 5,196,624; US 5,196,625; EP 364,012 B, 2/15/90; US 3,312,745; US 3,341,614; US 3,442,965; US 3,674,885; US 4,447,664; US 4,533,651; US 4,587,374; US 4,996,386; US 5,210,060; US 5,510,306; WO 95/17961, 7/6/95; WO 95/18084; US 5,510,306; US 5,087,788; 4,301,316; 4,301,317; 4,855,527; 4,870,038; 5,026,933; 5,625,105 and 4,973,788 are useful by way of background to the invention. The manufacture of alkylbenzenesulfonate surfactants has recently been reviewed. See Vol. 56 in "Surfactant Science" series, Marcel Dekker, New York, 1996, including in particular Chapter 2 entitled "Alkylarylsulfonates: History, Manufacture, Analysis and Environmental Properties", pages 39-108 which includes 297 literature references. Documents referenced herein are incorporated in their entirety.

SUMMARY OF THE INVENTION

The present invention relies on an unexpected discovery that forming an alcohol in a specific manner and using it to alkylate benzene, toluene or similar aromatics results in an unexpectedly superior alkylarenesulfonate surfactant product. The invention contradicts conventional wisdom which might suggest that the methods adopted are hardly practical for the purposes to which they are applied. For example, it would more commonly be expected that an olefin would be used directly for combining with benzene to make alkylate, rather than converting it first to an alcohol.

Accordingly the present invention includes a process for preparing modified alkylarenesulfonate surfactant, especially modified alkylbenzenesulfonate surfactant although modified alkyltoluenesulfonate surfactants and modified

alkylnaphthalenesulfonate surfactants can equally be produced, these surfactants being suitable for use in cleaning products, said process comprising (a) at least one step of providing an alcohol, e.g., an alcohol having molecular weight of preferably at least about 144 and preferably no more than about 298, more preferably from about 158 to about 242, wherein said step is selected from: (i) providing an alcohol by selective hydroformylation of Fischer-Tropsch olefins, skeletally isomerized linear olefins and mixtures thereof; and (ii) providing an alcohol by positionally nonselectively hydroformylating a linear olefin, e.g., a linear olefin having molecular weight of at least about 126 and no more than about 280; and (iii) providing an alcohol by reacting an alkyl Grignard and a methyl alkyl ketone; and (b) a monoalkylation step of reacting the alcohol of stage (a) with an aromatic hydrocarbon selected from benzene, toluene, naphthalene and mixtures thereof in the presence of a suitable alkylation catalyst. Preferred alkylation steps used herein have an internal isomer selectivity (IIS) as defined hereinafter of from 0 to about 40. Preferred catalysts in the alkylation include at least partially crystalline oxides of Si, Al or combinations thereof, especially certain zeolites in at least partially acidic form, such as at least partially dealuminized H-mordenites.

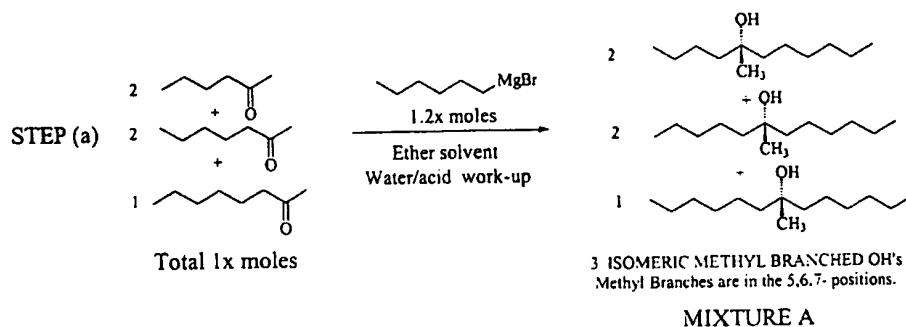
All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

Overall Process and Product

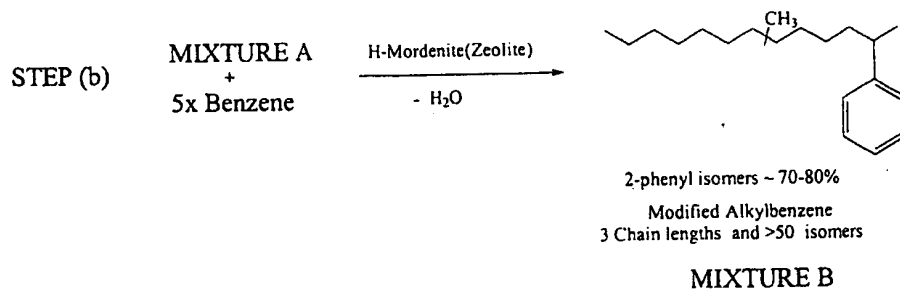
The present invention is well illustrated with reference to a particular embodiment. Thus, the present process can have a step, (a), of providing an alcohol or alcohol mixture having molecular weight of from about 144 to about 242. In general, suitable alcohol can be made by selective hydroformylation of Fischer-Tropsch olefins, or skeletally isomerized linear olefins, by positionally nonselectively hydroformylating linear olefins and by reactions of Grignard reagents or suitable equivalent organometallics such as organolithium reagents, with methyl alkyl ketones. The alcohol is alkylated in a particular manner. Typically the alkylate is sulfonated and neutralized and incorporated into cleaning products such as laundry detergents.

In the Grignard technique, a mixture of ketones such as 2-hexanone, 2-heptanone, and 2-octanone at a 2:2:1 mole ratio are reacted with an alkyl Grignard reagent such as hexylmagnesium bromide. On workup, a mixture of alcohols, in the case of this specific illustration 5-methyl-5-undecanol, 6-methyl-6-dodecanol and 7-methyl-7-tridecanol, is secured:

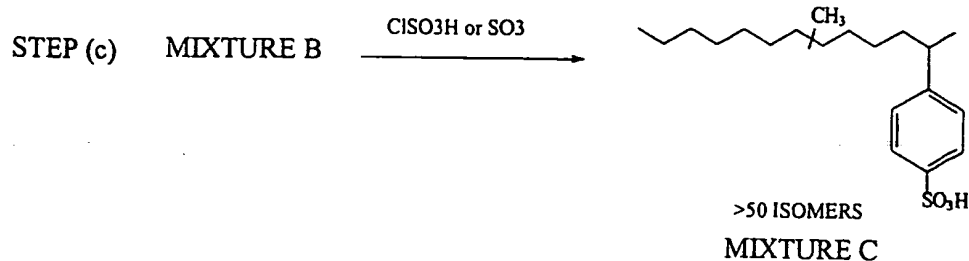


Note this process accomplishes the production of a methyl branched alcohol having a plurality of chainlengths, i.e., a series of homologs is present. It is preferred that the chain of the alcohol excluding methyl branches is from about 10 to about 14 carbon atoms in length.

The process continues with a monoalkylation step, (b), comprising reacting the alcohol of stage (a) with an aromatic hydrocarbon selected from benzene, toluene and mixtures thereof in the presence of an alkylation catalyst. A preferred catalyst is H-mordenite:



The modified alkylbenzene sulfonate produced in stage (b) of the present process is a novel composition in its own right. This material can (c) be sulfonated, for example using sulfur trioxide/air or using a molar equivalent of chlorosulfonic acid using methylene chloride as solvent:



The sulfonated product is a novel modified alkylbenzenesulfonate surfactant, which is particularly, lightly branched in consequence of its mode of preparation and has the form of a mixture which is high (>50%) in 2- + 3- phenyl isomer content. This mixture can be neutralized, e.g., with sodium, potassium, ammonium or substituted ammonium alkalis to form the corresponding salt, then mixed into a laundry detergent formulation.

Despite the seemingly illogical use of alcohols rather than olefins to make the products herein, the process of has some unique advantages, for example in that alcohols can be dehydrated, isomerized and alkylated herein all in one step. Moreover, alcohols can be conveniently made and used to conduct tailored batch syntheses of the present alkylbenzenesulfonates at relatively small scales using commercially available alcohols such as the LIAL™ types, ISALCHEM® and others, even when the corresponding olefins are not readily available in relatively small quantities. The present invention accordingly encompasses a method for prototyping the large-scale production of modified alkylarenesulfonate surfactants, said method comprising at least one step of making an alkylarene from an alcohol. This method is well illustrated by all the processes described herein.

The present process encompasses variations capable of giving an equivalent result. Importantly, this includes varying the source of the alcohol and the particulars of alkylation as now described in more detail:

(i) Alcohols by selective hydroformylation of Fischer-Tropsch olefins, or skeletally isomerized linear olefins and mixtures thereof

Alcohols suitable herein can be made by selectively hydroformylating Fischer-Tropsch olefins. Such alcohols are available from Sastech (South Africa). Suitable

processes for their manufacture are described in WO 97/01521. Alternatively, suitable alcohols are available as the products of dehydrating, using any conventional means, a skeletally isomerized mixture of linear olefins. A suitable skeletal isomerization is illustrated by skeletally isomerizing a mixture of 1-undecene, 1-dodecene and 1-tridecene over a Pt-SAPO catalyst. See US 5,082,956 and WO 95/21225 for more detail on such skeletal isomerizations and catalysts therefor.

Also it is contemplated herein that any such alcohols derived from different sources and processes can be blended in any proportions.

(ii) Alcohols by positionally nonselectively hydroformylating linear olefins

Alcohol mixtures suitable for use herein can alternatively be made by positionally nonselectively hydroformylating linear olefins. Optionally the alcohols can be separated by fractional crystallization to increase the content of the branched component. Suitable alcohols can be made by the hydroformylation and workup processes described in US 4,670,606. Other suitable alcohols made by this route are commercially available from Condea Augusta of Milan, Italy, also available in the U.S. through Condea Vista. These materials are known as ISALCHEM® alcohols.

Internal Isomer Selectivity and Selection of Alkylation Step

The present processes require an alkylation step having internal isomer selectivity in the range from 0 to 40, preferably from 0 to 20, more preferably still from 0 to 10. The Internal Isomer Selectivity or "IIS" as defined herein is measured for any given alkylation process step by conducting a test alkylation of benzene by 1-dodecene at a molar ratio of 10:1. The alkylation is conducted in the presence of an alkylation catalyst to a conversion of dodecene of at least 90% and formation of monophenyldodecanes of at least 60%. Internal isomer selectivity is then determined as:

$$\text{IIS} = 100 * \left(1 - \frac{\text{amount of terminal phenyldodecanes}}{\text{amount of total phenyldodecanes}} \right)$$

wherein amounts are amounts of the products by weight; the amount of terminal phenyldodecanes is the amount of the sum of 2-phenyldodecane and 3-phenyldodecane and the amount of total phenyldodecanes is the amount of the sum of 2-phenyldodecane and 3-phenyldodecane and 4-phenyldodecane and 5-phenyldodecane and 6-

phenyldodecane and wherein said amounts are determined by any known analytical technique for alkylbenzenesulfonates such as gas chromatography. See Analytical Chemistry, Nov. 1983, 55 (13), 2120-2126, Eganhouse et al, "Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography - high resolution gas chromatography and gas chromatography / mass spectrometry". In computing IIS according to the above formula, the amounts are divided before subtracting the result from 1 and multiplying by 100. It should of course be understood that the specific alkenes used to characterize or test any given alkylation step for suitability are reference materials permitting a comparison of the alkylation step herein with known alkylation steps as used in making linear alkylbenzenes and permitting the practitioner of the invention to decide if a given known alkylation step is, or is not, useful in the context of the series of process steps constituting the present invention. In the process of the invention as practiced, the hydrocarbon feedstock for alkylation actually used (in this invention, an alcohol) is of course that which is specified on the basis of the preceding process steps. Also to be noted, all the current commercial processes for LAS manufacture are excluded from the present invention solely on the basis of the IIS for the alkylation step. For example, LAS processes based on aluminum chloride, HF and the like all have IIS outside of the range specified for the instant process. In contrast, a few alkylation steps described in the literature but not currently applied in commercial alkylbenzenesulfonate production do have suitable IIS and are useful herein.

The better to assist the practitioner in determining IIS and in deciding whether a given alkylation process step is suitable for the purposes of the present invention, the following are more particular examples of IIS determination.

As noted, test alkylation of benzene by 1-dodecene is conducted at a mole ratio of 10:1 benzene to 1-dodecene and the alkylation is conducted in the presence of an alkylation catalyst to a conversion of dodecene of at least 90% and formation of monophenyldodecanes of at least 60%. The alkylation test must in general be conducted in a reaction time of less than 200 hours and at a reaction temperature of from about -15°C to about 500°C, preferably from about 20°C to 500°C. Pressure and catalyst concentration relative to 1-dodecene can vary widely. No solvent other than benzene is

used in the test alkylation. The process conditions used to determine the IIS for the catalyst or alkylation step in question can be based on the literature. The practitioner will use generally appropriate conditions based on a large body of well-documented data for alkylations. For example, appropriate process conditions to determine if an AlCl_3 alkylation can be used herein are exemplified by a reaction of 5 mole % AlCl_3 relative to 1-dodecene at 20-40°C for 0.5-1.0 hour in a batch reactor. Such a test demonstrates that an AlCl_3 alkylation step is unsuitable for use in the present process. An IIS of about 48 should be obtained. In another example, an appropriate test of alkylation using HF as a catalyst should give an IIS of about 60. Thus, neither AlCl_3 alkylation nor HF alkylation is within the scope of this invention. For a medium-pore zeolite such as a dealuminized mordenite, process conditions suitable for determining IIS are exemplified by passing 1-dodecene and benzene at a mole ratio of 10:1 across the mordenite catalyst at a WHSV of 30 Hr^{-1} at a reaction temperature of about 200°C and a pressure of about 200 psig which should give an IIS of about 0 for the mordenite catalyst. The temperatures and pressures for the exemplary mordenite alkylation test (see also the detailed examples of the instant process hereinafter) are expected to be more generally useful for testing zeolites and other shape-selective alkylation catalysts. Using a catalyst such as H-ZSM-4 one should obtain an IIS of about 18. Clearly both the dealuminized mordenite and H-ZSM-4 catalyzed alkylations give acceptable IIS for the invention, with the mordenite being superior.

Alkylation Catalyst

Accomplishing the required IIS in the alkylation process step is made possible by a tightly controlled selection of alkylation catalysts. Numerous alkylation catalysts are readily determined to be unsuitable. Unsuitable alkylation catalysts include the DETAL® process catalysts, aluminum chloride, HF, HF on zeolites, fluoridated zeolites, non-acidic calcium mordenite, and many others. Indeed no alkylation catalyst currently used for alkylation in the commercial production of detergent linear alkylbenzenesulfonates has yet been found suitable.

In contrast, suitable alkylation catalyst herein is selected from shape-selective moderately acidic alkylation catalysts, preferably zeolitic. The zeolite in such catalysts

for the alkylation step (step (b)) is preferably selected from the group consisting of mordenite, ZSM-4, ZSM-12, ZSM-20, offretite, gmelinite and zeolite beta in at least partially acidic form. More preferably, the zeolite in step (b) (the alkylation step) is substantially in acid form and is contained in a catalyst pellet comprising a conventional binder and further wherein said catalyst pellet comprises at least about 1 %, more preferably at least 5%, more typically from 50% to about 90%, of said zeolite.

More generally, suitable alkylation catalyst is typically at least partially crystalline, more preferably substantially crystalline not including binders or other materials used to form catalyst pellets, aggregates or composites. Moreover the catalyst is typically at least partially acidic. Fully exchanged Ca-form mordenite, for example, is unsuitable whereas H-form mordenite is suitable. This catalyst is useful for the alkylation step identified as step (b) in the claims hereinafter.

The pores characterizing the zeolites useful in the present alkylation process may be substantially circular, such as in cancrinite which has uniform pores of about 6.2 angstroms, or preferably may be somewhat elliptical, such as in mordenite. It should be understood that, in any case, the zeolites used as catalysts in the alkylation step of the present process have a major pore dimension intermediate between that of the large pore zeolites, such as the X and Y zeolites, and the relatively small pore size zeolites ZSM-5 and ZSM-11, and preferably between about 6A and about 7A. Indeed ZSM-5 has been tried and found inoperable in the present invention. The pore size dimensions and crystal structures of certain zeolites are specified in ATLAS OF ZEOLITE STRUCTURE TYPES by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association (1978 and more recent editions) and distributed by Polycrystal Book Service, Pittsburgh, Pa.

The zeolites useful in the alkylation step of the instant process generally have at least 10 percent of the cationic sites thereof occupied by ions other than alkali or alkaline-earth metals. Typical but non-limiting replacing ions include ammonium, hydrogen, rare earth, zinc, copper and aluminum. Of this group, particular preference is accorded ammonium, hydrogen, rare earth or combinations thereof. In a preferred embodiment, the zeolites are converted to the predominantly hydrogen form, generally

by replacement of the alkali metal or other ion originally present with hydrogen ion precursors, e.g., ammonium ions, which upon calcination yield the hydrogen form. This exchange is conveniently carried out by contact of the zeolite with an ammonium salt solution, e.g., ammonium chloride, utilizing well known ion exchange techniques. In certain preferred embodiments, the extent of replacement is such as to produce a zeolite material in which at least 50 percent of the cationic sites are occupied by hydrogen ions.

The zeolites may be subjected to various chemical treatments, including alumina extraction (dealumination) and combination with one or more metal components, particularly the metals of Groups IIB, III, IV, VI, VII and VIII. It is also contemplated that the zeolites may, in some instances, desirably be subjected to thermal treatment, including steaming or calcination in air, hydrogen or an inert gas, e.g. nitrogen or helium.

A suitable modifying treatment entails steaming of the zeolite by contact with an atmosphere containing from about 5 to about 100 percent steam at a temperature of from about 250 degree(s) to 1000 degree(s) C. Steaming may last for a period of between about 0.25 and about 100 hours and may be conducted at pressures ranging from sub-atmospheric to several hundred atmospheres.

In practicing the desired alkylation step of the instant process, it may be useful to incorporate the above-described intermediate pore size crystalline zeolites in another material, e.g., a binder or matrix resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica, and/or metal oxides. Matrix materials can be in the form of gels including mixtures of silica and metal oxides. The latter may be either naturally occurring or in the form of gels or gelatinous precipitates. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the intermediate pore size zeolites employed herein may be compounded with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, and silica-titania, as well as ternary combinations, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of finely divided zeolite and inorganic oxide gel matrix may vary widely, with the zeolite content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the composite.

A group of zeolites which includes some useful for the alkylation step herein have a silica:alumina ratio of at least 10:1, preferably at least 20:1. The silica:alumina ratios referred to in this specification are the structural or framework ratios, that is, the ratio for the SiO_4 to the AlO_4 tetrahedra. This ratio may vary from the silica:alumina ratio determined by various physical and chemical methods. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite, thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain treatments such as the dealuminization methods described below which result in the presence of ionic aluminum free of the zeolite structure are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined.

Zeolite beta suitable for use herein (but less preferred than H-mordenite) is disclosed in U.S. Pat. No. 3,308,069 to which reference is made for details of this zeolite and its preparation. Such a zeolite in the acid form is also commercially available as Zeocat PB/H from Zeochem.

When the zeolites have been prepared in the presence of organic cations they are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert

atmosphere at 540°C. for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 540°C. in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of the zeolite; but it does appear to favor the formation of this special type of zeolite. Some natural zeolites may sometimes be converted to zeolites of the desired type by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination. The zeolites preferably have a crystal framework density, in the dry hydrogen form, not substantially below about 1.6 g.cm⁻³. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W. M. Meier included in "Proceedings of the Conference on Molecular Sieves, London, April 1967", published by the Society of Chemical Industry, London, 1968. Reference is made to this paper for a discussion of the crystal framework density. A further discussion of crystal framework density, together with values for some typical zeolites, is given in U.S. Pat. No. 4,016,218, to which reference is made. When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. It has been found that although the hydrogen form of the zeolite catalyzes the reaction successfully, the zeolite may also be partly in the alkali metal form.

EP 466,558 describes an acidic mordenite type alkylation catalyst also of possible use herein having overall Si/Al atomic ratio of 15-85 (15-60), Na weight content of less than 1000 ppm (preferably less than 250 ppm), having low or zero content of extra-network Al species, and an elementary mesh volume below 2,760 nm³.

US 5,057,472 useful for preparing alkylation catalysts herein relates to concurrent dealumination and ion-exchange of an acid-stable Na ion-containing zeolite, preferably mordenite effected by contact with a 0.5-3 (preferably 1-2.5) M HNO₃ solution containing sufficient NH₄NO₃ to fully exchange the Na ions for NH₄ and H ions. The resulting zeolites can have an SiO₂:Al₂O₃ ratio of 15-26 (preferably 17-23):1 and are preferably calcined to at least partially convert the NH₄/H form to an H form. Optionally,

though not necessarily particularly desirable in the present invention, the catalyst can contain a Group VIII metal (and optionally also an inorganic oxide) together with the calcined zeolite of '472.

Another acidic mordenite catalyst useful for the alkylation step herein is disclosed in US 4,861,935 which relates to a hydrogen form mordenite incorporated with alumina, the composition having a surface area of at least 580 m² /g. Other acidic mordenite catalysts useful for the alkylation step herein include those described in US 5,243,116 and US 5,198,595. Yet another alkylation catalyst useful herein is described in US 5,175,135 which is an acid mordenite zeolite having a silica/alumina molar ratio of at least 50:1, a Symmetry Index of at least 1.0 as determined by X-ray diffraction analysis, and a porosity such that the total pore volume is in the range from about 0.18 cc/g to about 0.45 cc/g and the ratio of the combined meso- and macropore volume to the total pore volume is from about 0.25 to about 0.75.

Particularly preferred alkylation catalysts herein include the acidic mordenite catalysts ZeocatTM FM-8/25H available from Zeochem; CBV 90 A available from Zeolyst International, and LZM-8 available from UOP Chemical Catalysts.

Most generally, any alkylation catalyst may be used herein though very preferably, the alkylation step meets the internal isomer selectivity requirements identified supra.

Distillation of Modified Alkylbenzenes

Optionally, depending on feedstock and the precise sequence of steps used, the present process can include distillation of modified alkylbenzenes, for example to remove unreacted starting materials, alcohols, excesses of benzene and the like. Any conventional distillation apparatus can be used. The general practice is similar to that used for distillation of commercial linear alkylbenzenes (LAB). Suitable distillation steps are described in the hereinabove-referenced Surfactant Science Series review of alkylbenzenesulfonate manufacture.

Sulfonation and Workup

In general, sulfonation of the modified alkylbenzenes in the instant process can be accomplished using any of the well-known sulfonation systems, including those

described in the hereinabove-referenced volume "Detergent Manufacture Including Zeolite Builders and Other New Materials" as well as in the hereinabove-referenced Surfactant Science Series review of alkylbenzenesulfonate manufacture. Common sulfonation systems include sulfuric acid, chlorosulfonic acid, oleum, sulfur trioxide and the like. Sulfur trioxide/air is especially preferred. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in US 3,427,342, Chemithon.

Any convenient workup steps may be used in the present process. Common practice is to neutralize after sulfonation with any suitable alkali. Thus the neutralization step can be conducted using alkali selected from sodium, potassium, ammonium, magnesium and substituted ammonium alkalis and mixtures thereof. Potassium can assist solubility, magnesium can promote soft water performance and substituted ammonium can be helpful for formulating specialty variations of the instant surfactants. The invention encompasses any of these derivative forms of the modified alkylbenzenesulfonate surfactants as produced by the present process and their use in consumer product compositions.

Alternately the acid form of the present surfactants can be added directly to acidic cleaning products, or can be mixed with cleaning ingredients and then neutralized.

Post-alkylation steps

As noted, the process herein includes embodiments having steps that take place subsequent to the alkylation step (c). These steps preferably include (d) sulfonating the product of step (c); and one or more steps selected from (e) neutralizing the product of step (d); and (f) mixing the product of step (d) or (e) with one or more cleaning product adjunct materials; thereby forming a cleaning product.

Blended Embodiments

In one preferred embodiment, prior to the sulfonation step in the instant process, modified alkylbenzene which is the product of said step (b) is blended with a linear alkylbenzene, such as a linear C₁₀-C₁₄ alkylbenzene, produced by a conventional process. In another such embodiment, in any step subsequent to said sulfonation step (c), modified alkylbenzene sulfonate (acid-form or neutralized form) produced in accordance with the present process is blended with a linear alkylbenzene sulfonate, such as a linear

C₁₀-C₁₄ alkylbenzene sulfonate (acid-form or neutralized form) produced by a conventional process. In these blended embodiments, blends can be made at a weight ratio of the linear and modified alkylbenzenes or their derivatives of from 100:1 to 1:100. A preferred process has a ratio of modified alkylbenzene to linear alkylbenzene compounds of from about 10:90 to about 50:50. Another preferred process has a ratio of modified alkylbenzene to linear alkylbenzene compounds of from about 51:49 to about 92:8.

Urea Clathration or Sorptive Separation

In general, known separation techniques can be used at any stage in the instant processes to separate precursors to the present alcohols or the alcohols themselves. Separation techniques include the use of urea clathration and separation by sorption, for example on any suitable porous material, for example one based on pyrolyzed SARAN, or on a zeolite or aluminophosphate. When a sorptive method is used, there is a strong preference to use zeolites in such a form that chemical conversion, e.g., polymerization, is minimized.

Urea clathration can also be used herein as a step for separating alcohols or their olefinic precursors as is well known in the art. Suitable methods are as described in Surfactant Science Series, Marcel Dekker, N.Y., 1996, Vol. 56, , pages 9-10 and references therein. See also "Detergent Manufacture Including Zeolite Builders and other New Materials, Ed. Sittig., Noyes Data Corp., 1979, pages 25-30 and especially US 3,506,569 incorporated in its entirety which uses solid urea and no chlorocarbon solvents. More generally but less preferably, US 3,162,627 may be used. When conducting such separations, care is taken to eliminate residual urea, which can adversely affect alkylation.

Other Process Steps

Optionally any other process steps can be inserted between the essential steps in the instant process. Optional steps can further be inserted before or after the complete sequence of essential steps as defined herein. Other process steps can include, for example, at least partially dehydrating the alcohol in an additional step, inserted between steps (a) (the alcohol provision step or steps) and (b) (the alkylation step or steps).

Alternatively, a separation step or steps may be placed between steps (a) and (b). Such a separation step can be, for example, a sorptive separation step and/or a distillation step. Such steps can, for example, be useful for removing any identified impurities in the alcohol which may be known to adversely affect the alkylation catalyst's efficacy or lifetime.

Modified Alkylbenzenes and Alkylbenzenesulfonate Products

As noted in summary, the present invention relates to a process for preparing modified alkylbenzenesulfonate surfactant suitable for use in cleaning products such as laundry detergents, hard surface cleaners, dishwashing detergents and the like and to the products of such processes.

The term "modified alkylbenzenesulfonate surfactant" (MAS) refers to the product of the processes herein. The term "modified" as applied either to the novel alkylbenzenesulfonate surfactants or to the novel alkylbenzenes (MAB) is used as a qualifier to indicate that the product of the present process, especially when produced using an alkylation step having IIS of from 0 to 40, is compositionally different from that of all alkylbenzenesulfonate surfactants hitherto used in commerce. Most particularly, the instant compositions differ compositionally from the so-called "ABS" or poorly biodegradable alkylbenzenesulfonates, and from the so-called "LAS" or linear alkylbenzenesulfonate surfactants. Conventional LAS surfactants are currently commercially available through several processes including those relying on HF-catalyzed or aluminum chloride-catalyzed alkylation of benzene. Other commercial LAS surfactants include LAS made by the DETAL® process. The modified alkylbenzenesulfonate surfactants herein are also compositionally different from those made by alkylating linear olefins using fluoridated zeolite catalyst systems, including fluoridated mordenites. Without being limited by theory, it is believed that the modified alkylbenzenesulfonate surfactants herein are uniquely lightly branched. They typically contain a plurality of isomers and/or homologs. Often, this plurality of species (often tens or even hundreds) is accompanied by a relatively high total content of 2-phenyl isomers, 2-phenyl isomer contents at the very least exceeding current DETAL® process and commonly 50% or even 70% or higher being attained. Moreover the modified

alkylbenzenesulfonate products herein have advantageous isomer distributions and differ in physical properties from known alkylbenzenesulfonate surfactants, for example by having improved laundry/hard-surface cleaning performance and excellent mass efficiency in hard water.

Formulation into Cleaning Products

The present invention also encompasses a cleaning product formed by the instant process comprising:

- (a) from about 0.1% to about 99.8%, more typically up to about 50%, of modified alkylbenzenesulfonate surfactant as prepared herein and
- (b) from about 0.00001%, more typically at least about 1%, to about 99.9% of one or more of said cleaning product adjunct materials.

Adjunct materials can vary widely and accordingly can be used at widely ranging levels. For example, detergent enzymes such as proteases, amylases, cellulases, lipases and the like as well as bleach catalysts including the macrocyclic types having manganese or similar transition metals all useful in laundry and cleaning products can be used herein at very low, or less commonly, higher levels.

Other cleaning product adjunct materials suitable herein include bleaches, especially the oxygen bleach types including activated and catalyzed forms with such bleach activators as nonanoyloxybenzenesulfonate and/or tetraacetylenediamine and/or any of its derivatives or derivatives of phthaloylimidoperoxycaproic acid or other imido- or amido-substituted bleach activators including the lactam types, or more generally any mixture of hydrophilic and/or hydrophobic bleach activators (especially acyl derivatives including those of the C₆-C₁₆ substituted oxybenzenesulfonates); preformed peracids related to or based on any of the hereinbefore mentioned bleach activators, builders including the insoluble types such as zeolites including zeolites A, P and the so-called maximum aluminum P as well as the soluble types such as the phosphates and polyphosphates, any of the hydrous, water-soluble or water-insoluble silicates, 2,2'-oxydisuccinates, tartrate succinates, glycolates, NTA and many other ethercarboxylates or citrates, chelants including EDTA, S,S'-EDDS, DTPA and phosphonates, water-soluble polymers, copolymers and terpolymers, soil release polymers, cosurfactants

including any of the known anionic, cationic, nonionic or zwitterionic types, optical brighteners, processing aids such as crisping agents and fillers, solvents, antiredeposition agents, silicone/silica and other suds suppressors, hydrotropes, perfumes or pro-perfumes, dyes, photobleaches, thickeners, simple salts and alkalis such as those based on sodium or potassium including the hydroxides, carbonates, bicarbonates and sulfates and the like. When combined with the modified alkylbenzenesulfonate surfactants of the instant process, any of the anhydrous, hydrous, water-based or solvent-borne cleaning products are readily accessible as granules, liquids, tablets, powders, flakes, gels, extrudates, pouched or encapsulated forms or the like. Accordingly the present invention also includes the various cleaning products made possible or formed by any of the processes described. These may be used in discrete dosage forms, used by hand or by machine, or may be continuously dosed into all suitable cleaning appliances or delivery devices.

Cleaning Products in Detail

References cited herein are incorporated by reference. The surfactant compositions prepared by the processes of the present invention can be used in a wide range of consumer cleaning product compositions including powders, granules, gels, pastes, tablets, pouches, bars, types delivered in dual-compartment containers, spray or foam detergents and other homogeneous or multiphasic consumer cleaning product forms. They can be used or applied by hand and/or can be applied in unitary or freely alterable dosage, or by automatic dispensing means, or are useful in appliances such as washing-machines or dishwashers or can be used in institutional cleaning contexts, including for example, for personal cleansing in public facilities, for bottle washing, for surgical instrument cleaning or for cleaning electronic components. They can have a wide range of pH, for example from about 2 to about 12 or higher, and they can have a wide range of alkalinity reserve which can include very high alkalinity reserves as in uses such as drain unblocking in which tens of grams of NaOH equivalent can be present per 100 grams of formulation, ranging through the 1-10 grams of NaOH equivalent and the mild or low-alkalinity ranges of liquid hand cleaners, down to the acid side such as in

acidic hard-surface cleaners. Both high-foaming and low-foaming detergent types are encompassed.

Consumer product cleaning compositions are described in the "Surfactant Science Series", Marcel Dekker, New York, Volumes 1-67 and higher. Liquid compositions in particular are described in detail in the Volume 67, "Liquid Detergents", Ed. Kuo-Yann Lai, 1997, ISBN 0-8247-9391-9 incorporated herein by reference. More classical formulations, especially granular types, are described in "Detergent Manufacture including Zeolite Builders and Other New Materials", Ed. M. Sittig, Noyes Data Corporation, 1979 incorporated by reference. See also Kirk Othmer's Encyclopedia of Chemical Technology.

Consumer product cleaning compositions herein nonlimitingly include:

Light Duty Liquid Detergents (LDL): these compositions include LDL compositions having surfactancy improving magnesium ions (see for example WO 97/00930 A; GB 2,292,562 A; US 5,376,310; US 5,269,974; US 5,230,823; US 4,923,635; US 4,681,704; US 4,316,824; US 4,133,779) and/or organic diamines and/or various foam stabilizers and/or foam boosters such as amine oxides (see for example US 4,133,779) and/or skin feel modifiers of surfactant, emollient and/or enzymatic types including proteases; and/or antimicrobial agents; more comprehensive patent listings are given in Surfactant Science Series, Vol. 67, pages 240-248.

Heavy Duty Liquid Detergents (HDL): these compositions include both the so-called "structured" or multi-phase (see for example US 4,452,717; US 4,526,709; US 4,530,780; US 4,618,446; US 4,793,943; US 4,659,497; US 4,871,467; US 4,891,147; US 5,006,273; US 5,021,195; US 5,147,576; US 5,160,655) and "non-structured" or isotropic liquid types and can in general be aqueous or nonaqueous (see, for example EP 738,778 A; WO 97/00937 A; WO 97/00936 A; EP 752,466 A; DE 19623623 A; WO 96/10073 A; WO 96/10072 A; US 4,647,393; US 4,648,983; US 4,655,954; US 4,661,280; EP 225,654; US 4,690,771; US 4,744,916; US 4,753,750; US 4,950,424; US 5,004,556; US 5,102,574; WO 94/23009; and can be with bleach (see for example US 4,470,919; US 5,250,212; EP 564,250; US 5,264,143; US 5,275,753; US 5,288,746; WO 94/11483; EP 598,170; EP 598,973; EP 619,368; US 5,431,848; US 5,445,756) and/or

enzymes (see for example US 3,944,470; US 4,111,855; US 4,261,868; US 4,287,082; US 4,305,837; US 4,404,115; US 4,462,922; US 4,529,5225; US 4,537,706; US 4,537,707; US 4,670,179; US 4,842,758; US 4,900,475; US 4,908,150; US 5,082,585; US 5,156,773; WO 92/19709; EP 583,534; EP 583,535; EP 583,536; WO 94/04542; US 5,269,960; EP 633,311; US 5,422,030; US 5,431,842; US 5,442,100) or without bleach and/or enzymes. Other patents relating to heavy-duty liquid detergents are tabulated or listed in Surfactant Science Series, Vol. 67, pages 309-324.

Heavy Duty Granular Detergents (HDG): these compositions include both the so-called "compact" or agglomerated or otherwise non-spray-dried, as well as the so-called "fluffy" or spray-dried types. Included are both phosphated and nonphosphated types. Such detergents can include the more common anionic-surfactant based types or can be the so-called "high-nonionic surfactant" types in which commonly the nonionic surfactant is held in or on an absorbent such as zeolites or other porous inorganic salts. Manufacture of HDG's is, for example, disclosed in EP 753,571 A; WO 96/38531 A; US 5,576,285; US 5,573,697; WO 96/34082 A; US 5,569,645; EP 739,977 A; US 5,565,422; EP 737,739 A; WO 96/27655 A; US 5,554,587; WO 96/25482 A; WO 96/23048 A; WO 96/22352 A; EP 709,449 A; WO 96/09370 A; US 5,496,487; US 5,489,392 and EP 694,608 A.

"Softergents" (STW): these compositions include the various granular or liquid (see for example EP 753,569 A; US 4,140,641; US 4,639,321; US 4,751,008; EP 315,126; US 4,844,821; US 4,844,824; US 4,873,001; US 4,911,852; US 5,017,296; EP 422,787) softening-through-the wash types of product and in general can have organic (e.g., quaternary) or inorganic (e.g., clay) softeners.

Hard Surface Cleaners (HSC): these compositions include all-purpose cleaners such as cream cleansers and liquid all-purpose cleaners; spray all-purpose cleaners including glass and tile cleaners and bleach spray cleaners; and bathroom cleaners including mildew-removing, bleach-containing, antimicrobial, acidic, neutral and basic types. See, for example EP 743,280 A; EP 743,279 A. Acidic cleaners include those of WO 96/34938 A.

Bar Soaps and/or Laundry Bars (BS&HW): these compositions include personal cleansing bars as well as so-called laundry bars (see, for example WO 96/35772 A); including both the syndet and soap-based types and types with softener (see US 5,500,137 or WO 96/01889 A); such compositions can include those made by common soap-making techniques such as plodding and/or more unconventional techniques such as casting, absorption of surfactant into a porous support, or the like. Other bar soaps (see for example BR 9502668; WO 96/04361 A; WO 96/04360 A; US 5,540,852) are also included. Other handwash detergents include those such as are described in GB 2,292,155 A and WO 96/01306 A.

Shampoos and Conditioners (S&C): (see, for example WO 96/37594 A; WO 96/17917 A; WO 96/17590 A; WO 96/17591 A). Such compositions in general include both simple shampoos and the so-called "two-in-one" or with conditioner" types.

Liquid Soaps (LS): these compositions include both the so-called "antibacterial" and conventional types, as well as those with or without skin conditioners and include types suitable for use in pump dispensers, and by other means such as wall-held devices used institutionally.

Special Purpose Cleaners (SPC): including home dry cleaning systems (see for example WO 96/30583 A; WO 96/30472 A; WO 96/30471 A; US 5,547,476; WO 96/37652 A); bleach pretreatment products for laundry (see EP 751,210 A); fabric care pretreatment products (see for example EP 752,469 A); liquid fine fabric detergent types, especially the high-foaming variety; rinse-aids for dishwashing; liquid bleaches including both chlorine type and oxygen bleach type, and disinfecting agents, mouthwashes, denture cleaners (see, for example WO 96/19563 A; WO 96/19562 A), car or carpet cleaners or shampoos (see, for example EP 751,213 A; WO 96/15308 A), hair rinses, shower gels, foam baths and personal care cleaners (see, for example WO 96/37595 A; WO 96/37592 A; WO 96/37591 A; WO 96/37589 A; WO 96/37588 A; GB 2,297,975 A; GB 2,297,762 A; GB 2,297,761 A; WO 96/17916 A; WO 96/12468 A) and metal cleaners; as well as cleaning auxiliaries such as bleach additives and "stain-stick" or other pre-treat types including special foam type cleaners (see, for example EP 753,560 A; EP 753,559 A; EP 753,558 A; EP 753,557 A; EP 753,556 A) and anti-sunfade

treatments (see WO 96/03486 A; WO 96/03481 A; WO 96/03369 A) are also encompassed.

Detergents with enduring perfume (see for example US 5,500,154; WO 96/02490) are increasingly popular.

Other preferred embodiments

While the invention is well described hereinabove, the following aspects and embodiments are of interest. The invention encompasses preferred processes wherein said aromatic hydrocarbon is exclusively benzene: these are the most widely useful. The invention also includes corresponding modified alkylbenzenes and alkyltoluenes produced by the process. Alternatively, modified alkyltoluenes or alkyl naphthalenes and the corresponding sulfonated derivatives in any suitable form. Suitable forms of any of the surfactant produced herein include the acid form, the sodium salt form, the potassium salt form, the ammonium form, and the substituted ammonium form: all can be produced and are equally encompassed herein.

Preferred alcohols can have molecular weight of from about 144 to about 298 and, when said step a(ii) is used to provide said alcohol, suitable linear olefins can have a molecular weight of from about 126 to about 280. As discussed hereinabove, preferred processes include those wherein the alkylation step has an internal isomer selectivity of from 0 to 40, more preferably 20 or lower. Generally the alkylation step herein is a monoalkylation step, though some dialkylation byproduct, for example to a maximum of about 5% by weight is acceptable, depending on the intended use. For laundry cleaning products, it is preferred to use compositions having a minimum of dialkylation.

The invention, as noted, encompasses cleaning products, especially laundry detergents, produced by the processes. Certain preferred cleaning products comprise from about 1% to about 30% of said modified alkylbenzenesulfonate surfactant and from about 10% to about 99% of cleaning product adjunct materials such as at least one member selected from the group consisting of detergents, enzymes, bleaches, surfactants other than said modified alkylbenzenesulfonate surfactant, builders, polymers, brighteners, perfumes and mixtures thereof.

Also, the processes herein preferably include use in the alkylation step of an alkylation catalyst selected from at least partially dealuminized, at least partially acidic mordenites, at least partially acidic zeolite beta and mixtures thereof, more preferably, at least partially dealuminized, at least partially acidic mordenite catalysts, more preferably still, dealuminized H-mordenites. Clearly, based on the components reacted and the products formed, processes are encompassed wherein said alkylation step both dehydrates and alkylates said alcohol. Processes are encompassed wherein said alkylation step is conducted at temperatures in the range from about 150°C to about 220°C. Preferred processes include those wherein said alcohol is provided by means of Grignard reaction., for example reacting n-hexylmagnesium bromide with a mixture of 2-hexanone, 2-heptanone and 2-octanone.

The invention is further nonlimitingly illustrated by the following examples. All amounts and proportions are by weight unless otherwise noted.

EXAMPLE 1

Modified alkylbenzene sulfonate surfactant prepared via specific tertiary alcohol mixture from a Grignard reaction

A mixture of 5-methyl-5-undecanol, 6-methyl-6-dodecanol and 7-methyl-7-tridecanol is prepared via the following Grignard reaction. A mixture of 28g of 2-hexanone, 28g of 2-heptanone, 14g of 2-octanone and 100g of diethyl ether are added to an addition funnel. The ketone mixture is then added dropwise over a period of 1.75 hours to a nitrogen blanketed stirred three neck round bottom flask, fitted with a reflux condenser and containing 350 mL of 2.0 M n-hexylmagnesium bromide in diethyl ether and an additional 100 mL of diethyl ether. After the addition is complete the reaction mixture is stirred an additional 1 hour at 20°C. The reaction mixture is then added to 600g of a mixture of ice and water with stirring. To this mixture is added 228.6g of 30% sulfuric acid solution. The resulting two liquid phases are added to a separatory funnel. The aqueous layer is drained and the remaining ether layer is washed twice with 600 mL of water. The ether layer is then evaporated under vacuum to yield 115.45g of the desired alcohol mixture. A 5g sample of the light yellow alcohol mixture is added to a glass autoclave liner along with 70 mL of benzene and 1 g of a shape selective zeolite

catalyst (acidic mordenite catalyst ZeocatTM FM-8/25H). The glass liner is sealed inside a stainless steel, rocking autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 1000 psig N₂. With mixing, the mixture is heated to 180-190°C overnight for 14-15 hours at which time it is then cooled and removed from the autoclave. The reaction mixture is filtered to remove catalyst and concentrated by evaporation of benzene using rotary evaporator to obtain a clear colorless or nearly colorless liquid product. The modified alkylbenzene mixture is then sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed, the product neutralized with sodium methoxide in methanol and the methanol evaporated to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 2

Modified alkylbenzene sulfonate prepared via an alcohol derived from a positionally nonselectively hydroformylated linear olefin.

A 5g sample of ISALCHEM 123(R) (ENICHEM) is added to a glass autoclave liner along with 70 mL of benzene and 1 g of a shape selective zeolite catalyst (acidic mordenite catalyst Zeocat(R) FM-8/25H). The glass liner is sealed inside a stainless steel, rocking autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 1000 psig N₂. With mixing, the mixture is heated to 180-200°C overnight for 14-15 hours at which time it is then cooled and removed from the autoclave. The reaction mixture is filtered to remove catalyst and concentrated by evaporation of benzene using rotary evaporator to obtain a clear colorless or nearly colorless liquid product. The modified alkylbenzene mixture is then sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed, the product neutralized with sodium methoxide in methanol and the methanol evaporated to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 3

Modified alkylbenzene sulfonate prepared via lightly branched alcohol prepared from zeolite-catalyzed oligomerization of propylene-containing lower olefins.

Step (a)

A lightly branched olefin mixture is prepared and isolated according to US 5,026,933 Example XVI. The olefin mixture is converted to a lightly branched primary alcohol mixture via hydroformylation chemistry according to the Example numbered as No. 2 in US 5,245,072.

Step (b)

To a glass autoclave liner is added 1 mole equivalent of the lightly branched alcohol mixture, 20 mole equivalents of benzene and 20 wt. % ,based on the alcohol mixture, of a shape selective zeolite catalyst (acidic mordenite catalyst Zeocat^(R) FM-8/25H). The glass liner is sealed inside a stainless steel, rocking autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 1000 psig N₂. With mixing, the mixture is heated to 170-190°C overnight for 14-15 hours at which time it is then cooled and removed from the autoclave. The reaction mixture is filtered to remove catalyst and concentrated by evaporation of benzene using rotary evaporator to obtain a clear colorless or nearly colorless liquid product.

Step (c)

The lightly branched alkylbenzene mixture is then sulfonated with an equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed, the product neutralized with sodium methoxide in methanol and the methanol evaporated to give modified alkylbenzene sulfonate, sodium salt.

EXAMPLE 4

Cleaning Composition

The procedure of Example 3 is repeated with the final product of step (c) being further treated by the following additional step:

Step (d): Incorporation of the product of step (c) into a cleaning composition

10% by weight of the product of step (c) is combined with 90% by weight of an agglomerated compact laundry detergent granule.

EXAMPLE 5

Cleaning Composition

The procedure of any of Examples 1-2 or 6 is repeated and the final product is further treated by the following additional step:

Incorporation of modified alkylbenzenesulfonate into a cleaning composition

10% by weight of the product of the modified alkylbenzenesulfonate is combined with 90% by weight of an agglomerated compact laundry detergent granule.

EXAMPLE 6

Modified alkylbenzene sulfonate surfactant prepared via specific tertiary alcohol mixture from a Grignard reaction

A mixture of 5-methyl-5-undecanol, 6-methyl-6-dodecanol and 7-methyl-7-tridecanol is prepared via the following Grignard reaction. A mixture of 28g of 2-hexanone, 28g of 2-heptanone, 14g of 2-octanone and 100g of diethyl ether are added to an addition funnel. The ketone mixture is then added dropwise over a period of 1.75 hours to a nitrogen blanketed stirred three neck round bottom flask, fitted with a reflux condenser and containing 350 mL of 2.0 M hexylmagnesium bromide in diethyl ether and an additional 100 mL of diethyl ether. After the addition is complete, the reaction mixture is stirred an additional 1 hour at 20°C. The reaction mixture is then added to 600g of a mixture of ice and water with stirring. To this mixture is added 228.6g of 30% sulfuric acid solution. The resulting two liquid phases are added to a separatory funnel. The aqueous layer is drained and the remaining ether layer is washed twice with 600 mL of water. The ether layer is then evaporated under vacuum to yield 115.45g of the desired alcohol mixture. A 100g sample of the light yellow alcohol mixture is added to a glass autoclave liner along with 300 mL of benzene and 20g of a shape selective zeolite catalyst (acidic mordenite catalyst ZeocatTM FM-8/25H). The glass liner is sealed inside a stainless steel, rocking autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 1000 psig N₂. With mixing, the mixture is heated to 170°C overnight for 14-15 hours at which time it is then cooled and removed from the autoclave. The reaction mixture is filtered to remove catalyst and concentrated by distilling off the

benzene which is dried and recycled. A clear colorless or nearly colorless lightly branched olefin mixture is obtained.

50g of the lightly branched olefin mixture provided by dehydrating the Grignard alcohol mixture as above is added to a glass autoclave liner along with 150 mL of benzene and 10 g of a shape selective zeolite catalyst (acidic mordenite catalyst ZeocatTM FM-8/25H). The glass liner is sealed inside a stainless steel, rocking autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 1000 psig N₂. With mixing, the mixture is heated to 195°C overnight for 14-15 hours at which time it is then cooled and removed from the autoclave. The reaction mixture is filtered to remove catalyst and concentrated by distilling off the benzene which is dried and recycled. A clear colorless or nearly colorless liquid product is obtained. The product is distilled under vacuum (1-5 mm of Hg) and the fraction from 95°C - 135°C is retained.

The retained fraction, i.e., the modified alkylbenzene mixture, is then sulfonated with a molar equivalent of SO₃ and the resulting product is neutralized with sodium methoxide in methanol and the methanol evaporated to give the modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 7

Cleaning Product Compositions

In this Example, the following abbreviation is used for a modified alkylbenzene sulfonate, sodium salt form or potassium salt form, prepared according to any of the preceding process examples, e.g., Example 6: MAS

The following abbreviations are used for cleaning product adjunct materials:

Amylase	Amylolytic enzyme, 60KNU/g, NOVO, Termamyl® 60T
APA	C8-C10 amido propyl dimethyl amine
Bicarbonate	Sodium bicarbonate, anhydrous, 400µm - 1200µm
Borax	Na tetraborate decahydrate
Brightener 1	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino stilbene-2:2'-disulfonate
C45AS	C ₁₄ -C ₁₅ linear alkyl sulfate, Na salt
CaCl ₂	Calcium chloride
Carbonate	Na ₂ CO ₃ anhydrous, 200µm - 900µm

Cellulase	Cellulolytic enzyme, 1000 CEVU/g, NOVO, Carezyme®
Citrate	Trisodium citrate dihydrate, 86.4%, 425 µm - 850 µm
Citric Acid	Citric Acid, Anhydrous
CMC	Sodium carboxymethyl cellulose
CxyAS	C _{1x} -C _{1y} alkyl sulfate, Na salt or other salt if specified
CxyEz	C _{1x-1y} branched primary alcohol ethoxylate (average z moles of ethylene oxide)
CxyEzS	C _{1x} -C _{1y} alkyl ethoxylate sulfate, Na salt (average z moles of ethylene oxide; other salt if specified)
CxyFA	C _{1x} -C _{1y} fatty acid
Diamine	Alkyl diamine, e.g., 1,3 propanediamine, Dytek EP, Dytek A, (Dupont)
Dimethicone	40(gum)/60(fluid) wt. blend of SE-76 dimethicone gum (G.E Silicones Div.) / dimethicone fluid of viscosity 350 cS.
DTPA	Diethylene triamine pentaacetic acid
DTPMP	Diethylene triamine penta (methylene phosphonate), Monsanto (Dequest 2060)
Endolase	Endoglucanase, activity 3000 CEVU/g, NOVO
EtOH	Ethanol
Fatty Acid (C12/14)	C12-C14 fatty acid
Fatty Acid (RPS)	Rapeseed fatty acid
Fatty Acid (TPK)	Topped palm kernel fatty acid
HEDP	1,1-hydroxyethane diphosphonic acid
Isofol 16	C16 (average) Guerbet alcohols (Condea)
LAS	Linear Alkylbenzene Sulfonate (C11.8, Na or K salt)
Lipase	Lipolytic enzyme, 100kLU/g, NOVO, Lipolase®
LMFAA	C12-14 alkyl N-methyl glucamide
LMFAA	C12-14 alkyl N-methyl glucamide
MA/AA	Copolymer 1:4 maleic/acrylic acid, Na salt, avg. mw. 70,000.
MBAE _x	Mid-chain branched primary alkyl ethoxylate (average total carbons = x; average EO = 8)
MBAE _x S _z	Mid-chain branched primary alkyl ethoxylate sulfate, Na salt (average total carbons = z; average EO = x)
MBAS _x	Mid-chain branched primary alkyl sulfate, Na salt (average total carbons = x)
MEA	Monoethanolamine

MES	Alkyl methyl ester sulfonate, Na salt
MgCl ₂	Magnesium chloride
MnCAT	Macrocyclic Manganese Bleach Catalyst as in EP 544,440 A or, preferably, use [Mn(Bcyclam)Cl ₂] wherein Bcyclam = 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane or a comparable bridged tetra-aza macrocycle
NaDCC	Sodium dichloroisocyanurate
NaOH	Sodium hydroxide
NaPS	Paraffin sulfonate, Na salt
NaSKS-6	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
NaTS	Sodium toluene sulfonate
NOBS	Nonanoyloxybenzene sulfonate, sodium salt
LOBS	C12 oxybenzenesulfonate, sodium salt
PAA	Polyacrylic Acid (mw = 4500)
PAE	Ethoxylated tetraethylene pentamine
PAEC	Methyl quaternized ethoxylated dihexylene triamine
PBI	Anhydrous sodium perborate bleach of nominal formula NaBO ₂ ·H ₂ O ₂
PEG	Polyethylene glycol (mw=4600)
Percarbonate	Sodium Percarbonate, nominal formula 2Na ₂ CO ₃ ·3H ₂ O ₂
PG	Propanediol
Photobleach	Sulfonated Zinc Phthalocyanine encapsulated in dextrin soluble polymer
PIE	Ethoxylated polyethyleneimine
Protease	Proteolytic enzyme, 4KNPU/g, NOVO, Savinase®
QAS	R ₂ ·N ⁺ (CH ₃) _x ((C ₂ H ₄ O) _y H) _z with R ₂ = C ₈ - C ₁₈ x+z = 3, x = 0 to 3, z = 0 to 3, y = 1 to 15.
SAS	Secondary alkyl sulfate, Na salt
Silicate	Sodium Silicate, amorphous (SiO ₂ :Na ₂ O; 2.0 ratio)
Silicone antifoam	Polydimethylsiloxane foam controller + siloxane-oxyalkylene copolymer as dispersing agent; ratio of foam controller:dispersing agent = 10:1 to 100:1.
SRP 1	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	Sulfonated ethoxylated terephthalate polymer
SRP 3	Methyl capped ethoxylated terephthalate polymer

STPP	Sodium tripolyphosphate, anhydrous
Sulfate	Sodium sulfate, anhydrous
TAED	Tetraacetythylenediamine
TFA	C16-18 alkyl N-methyl glucamide
Zeolite A	Hydrated Sodium Aluminosilicate, $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$; 0.1 – 10 μm
Zeolite MAP	Zeolite (Maximum aluminum P) detergent grade (Crosfield)

The example is illustrative of the present invention, but is not meant to limit or otherwise define its scope. All parts, percentages and ratios used are expressed as percent weight unless otherwise noted. The following laundry detergent compositions A to E are prepared in accordance with the invention:

	A	B	C	D	E
MAS	22	16.5	11	1 - 5.5	10 - 25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES MBAS16.5 MBAE2S15.5	0	1 - 5.5	11	16.5	0 - 5
QAS	0 - 2	0 - 2	0 - 2	0 - 2	0 - 4
C23E6.5 or C45E7	1.5	1.5	1.5	1.5	0 - 4
Zeolite A	27.8	0	27.8	27.8	20 - 30
Zeolite MAP	0	27.8	0	0	0
PAA	2.3	2.3	2.3	2.3	0 - 5
Carbonate	27.3	27.3	27.3	27.3	20 - 30
Silicate	0.6	0.6	0.6	0.6	0 - 2
PB1	1.0	1.0	0-10	0-10	0 - 10
NOBS	0-1	0-1	0-1	0.1	0.5-3
LOBS	0	0	0-3	0	0
TAED	0	0	0	2	0
MnCAT	0	0	0	0	2ppm
Protease	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Cellulase	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.5
Amylase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 1
SRP 1 or SRP 2	0.4	0.4	0.4	0.4	0 - 1
Brightener 1 or 2	0.2	0.2	0.2	0.2	0 - 0.3

PEG	1.6	1.6	1.6	1.6	0 - 2
Silicone Antifoam	0.42	0.42	0.42	0.42	0 - 0.5
Sulfate, Moisture & Minors	---Balance---				
Density (g/L)	663	663	663	663	600 - 700

EXAMPLE 8**Cleaning Product Compositions**

The following liquid laundry detergent compositions F to J are prepared in accord with the invention. Abbreviations are as used in the preceding Examples.

	F	G	H	I	J
MAS	1 - 7	7 - 12	12 - 17	17 - 22	1 - 35
Any combination of: C25 AExS*Na (x = 1.8 - 2.5) MBAE1.8S15.5 MBAS15.5 C25 AS (linear to high 2-alkyl) C14-17 NaPS C12-16 SAS C18 1,4 disulfate LAS C12-16 MES	15 - 21	10 - 15	5 - 10	0 - 5	0 - 25
LMFAA	0 - 3.5	0 - 3.5	0 - 3.5	0 - 3.5	0 - 8
C23E9 or C23E6.5	0 - 2	0 - 2	0 - 2	0 - 2	0 - 8
APA	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 2
Citric Acid	5	5	5	5	0 - 8
Fatty Acid (TPK or C12/14)	2	2	2	2	0 - 14
EtOH	4	4	4	4	0 - 8
PG	6	6	6	6	0 - 10
MEA	1	1	1	1	0 - 3
NaOH	3	3	3	3	0 - 7
Na TS	2.3	2.3	2.3	2.3	0 - 4
Na formate	0.1	0.1	0.1	0.1	0 - 1
Borax	2.5	2.5	2.5	2.5	0 - 5
Protease	0.9	0.9	0.9	0.9	0 - 1.3
Lipase	0.06	0.06	0.06	0.06	0 - 0.3
Amylase	0.15	0.15	0.15	0.15	0 - 0.4
Cellulase	0.05	0.05	0.05	0.05	0 - 0.2
PAE	0 - 0.6	0 - 0.6	0 - 0.6	0 - 0.6	0 - 2.5
PIE	1.2	1.2	1.2	1.2	0 - 2.5
PAEC	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 2

SRP 2	0.2	0.2	0.2	0.2	0 - 0.5
Brightener 1 or 2	0.15	0.15	0.15	0.15	0 - 0.5
Silicone antifoam	0.12	0.12	0.12	0.12	0 - 0.3
Fumed Silica	0.0015	0.0015	0.0015	0.0015	0-0.003
Perfume	0.3	0.3	0.3	0.3	0 - 0.6
Dye	0.0013	0.0013	0.0013	0.0013	0-0.003
Moisture/minors	Balance	Balance	Balance	Balance	Balance
Product pH (10% in DI water)	7.7	7.7	7.7	7.7	6 - 9.5

What is claimed is:

1. A process for preparing modified alkylarene surfactants suitable for use in cleaning products, said process comprising:
 - (a) at least one step of providing an alcohol wherein said step is selected from:
 - (i) providing an alcohol by selective hydroformylation of Fischer-Tropsch olefins, skeletally isomerized linear olefins and mixtures thereof;
 - (ii) providing an alcohol by positionally nonselectively hydroformylating a linear olefin; and
 - (iii) providing an alcohol by reacting an alkyl Grignard and a methyl alkyl ketone;and
 - (b) a monoalkylation step of reacting the alcohol of step (a) with an aromatic hydrocarbon selected from benzene, toluene, naphthalene and mixtures thereof in the presence of an alkylation catalyst.
2. A process according to Claim 1 wherein said monoalkylation step has an internal isomer selectivity of from 0 to 40.
3. A process according to any of Claims 1 to 2 having the additional steps, of
 - (c) sulfonating the product of step (b); and
 - (d) neutralizing the product of step (c).
4. A process for preparing cleaning products, said process comprising:
 - (a) at least one step of providing an alcohol wherein said step is selected from:
 - (i) providing an alcohol by selective hydroformylation of Fischer-Tropsch olefins, skeletally isomerized linear olefins and mixtures thereof;
 - (ii) providing an alcohol by positionally nonselectively hydroformylating a linear olefin; and
 - (iii) providing an alcohol by reacting an alkyl Grignard and a methyl alkyl ketone;and
 - (b) a monoalkylation step of reacting the alcohol of stage (a) with an aromatic hydrocarbon selected from benzene, toluene, naphthalene and mixtures thereof in the presence of an alkylation catalyst.
 - (c) sulfonating the product of step (b);
 - (d) neutralizing the product of step (c); and

- (e) mixing the product of step (c) or (d) with one or more cleaning product adjunct materials; thereby forming a cleaning product.
5. A process according to any one of Claims 1 to 4 wherein said alkylation step uses an alkylation catalyst selected from at least partially dealuminized, at least partially acidic mordenites, at least partially acidic zeolite beta and mixtures thereof.
6. A process according to any one of Claims 1 to 5 wherein said alkylation step uses an at least partially dealuminized, at least partially acidic mordenite catalyst.
7. A process according to any one of Claims 1 to 6 wherein said alkylation step uses a dealuminized H-mordenite.
8. A process according to any one of Claims 1 to 7 wherein said alkylation step is conducted at temperatures in the range from about 150°C to about 220°C.
9. A modified alkylbenzenesulfonate surfactant or modified alkyltoluene surfactant produced by a process according to any of Claims 1 to 3 and 5 to 8.
10. A cleaning product produced according to any one of Claims 4 to 8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/01097

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C29/16 C07C29/40 C07C31/125 C07C2/66 C07C15/107
C07C303/06 C07C303/08 C07C309/31 C11D1/22

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 97 01521 A (SASTECH (PTY)) 16 January 1997 cited in the application see the whole document ---	1
A	US 5 245 072 A (T.J. GIACOBBE, ET AL.) 14 September 1993 cited in the application see example 2 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/01097

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: al Application No
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